PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2004-074138
(43)Date of publication of application : 11.03.2004

(51)Int.Cl. B01J 23/58
B01D 53/94
F01N 3/10
F01N 3/20
F02D 41/04

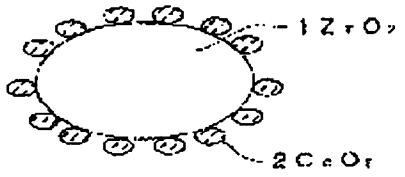
(21)Application number : 2002-285223
(22)Date of filing : 30.09.2002

(71)Applicant : TOYOTA MOTOR CORP
(72)Inventor : HARA NAOYUKI

(30)Priority
Priority number : 2002175830 Priority date : 17.06.2002 Priority country : JP

(54) CATALYST FOR EXHAUST GAS PURIFICATION, AND EXHAUST GAS PURIFICATION METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To suppress the granular growth of noble metals using cerium oxide and to prevent lowering of NOx purification rate.
SOLUTION: A noble metal is carried on an oxide carrier containing cerium-based compound oxide particles of an ununiform constitution having a large amount of CeO2 on the surface and less in the inner part. The granular growth the noble metal is suppressed by CeO2 much existing on the surface. The absolute amount of CeO2 is less than that in the conventional case, as the content of CeO2 in the inner part is small, causing less capacity of oxygen storing and releasing. This suppresses the consumption of a reducing component in rich spiking, to suppress the lowering of the NOx purification rate.



LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of

rejection]

[Date of extinction of right]

* NOTICES *

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1]
They are noble metals and NOx to oxide support. NOx which comes to support occlusion material In the catalyst for emission gas purification of an occlusion reduction type,
For this oxide support, CeO2 is the catalyst for emission gas purification characterized by including the Seria system multiple oxide particle of little [inside] heterogeneity structure many to a front face.
[Claim 2]
Said Seria system multiple oxide is a catalyst for emission gas purification according to claim 1 which is CeO2-ZrO2 multiple oxide.
[Claim 3]
Said noble metals are catalysts for emission gas purification according to claim 1 currently supported by said Seria system multiple oxide particle at least.
[Claim 4]
Said Seria system multiple oxide particle is a catalyst for emission gas purification according to claim 1 that to the exhaust gas downstream included. [than the exhaust gas upstream] [more]
[Claim 5]
The catalyst for emission gas purification according to claim 1 to 4 is contacted to the exhaust gas discharged from the lean-burn engine with which it is operated by 15 or more fuel lean atmosphere, and an air-fuel ratio (A/F) is intermittently made into a SUTOIKI - fuel rich ambient atmosphere. NOx contained in this exhaust gas It is this NOx at the Lean side. Occlusion is carried out to occlusion material and it is this NOx at a rich side from SUTOIKI. NOx emitted from occlusion material The emission-gas-purification approach characterized by returning.
[Claim 6]
Said fuel lean atmosphere is the emission-gas-purification approach according to claim 5 that an air-fuel ratio (A/F) is 18 or more.

[Translation done.]

* NOTICES *

JPO and NCIPI are not responsible for any
damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention is NOx used in the exhaust gas with which the lean atmosphere of hyperoxia and the rich ambient atmosphere where a reduction component is superfluous are changed by turns. It is related with the emission-gas-purification approach using the catalyst for emission gas purification and its catalyst for emission gas purification of an occlusion reduction type.
[0002]
[Description of the Prior Art]
The lean burn engine which burns in the lean atmosphere of hyperoxia is used for the automobile in recent years for the purpose of control of discharge of a carbon dioxide with improvement in fuel consumption. However, with a three way component catalyst general since the exhaust gas from a lean burn engine is the lean atmosphere of hyperoxia, purification of HC and CO is NOx, although it is possible. Reduction purification is difficult.
[0003]
Then, they are noble metals and NOx to oxide support. NOx which comes to support occlusion material An occlusion reduction type catalyst is developed and it is used under the combustion conditions which change by turns lean atmosphere with superfluous air, and the rich ambient atmosphere where a fuel is superfluous. Since the combustion gas in lean atmosphere with superfluous air is the lean atmosphere of hyperoxia, NO in exhaust gas is NO2 by oxidation. It becomes and is NOx. Occlusion is carried out to occlusion material as a nitrate etc. And the combustion gas of the rich ambient atmosphere where a fuel is superfluous is NOx by which is the rich ambient atmosphere where a reduction component is superfluous, and occlusion was carried out under the ambient atmosphere. NOx It is returned and purified to N2 by the reduction component which is emitted from occlusion material and exists in an ambient atmosphere at abundance.
[0004]
And in order to attain the purpose of the improvement in fuel consumption, and discharge control of a carbon dioxide, it is necessary to lengthen burn time in lean atmosphere with superfluous air, and to shorten burn time in the rich ambient atmosphere where a fuel is superfluous, and what (rich spike) it is made to burn in lean atmosphere and the rich ambient atmosphere where a fuel is superfluous is always introduced for in pulse is performed. However, since it is a hot oxidizing atmosphere, the combustion gas in lean atmosphere with superfluous air is NOx. Grain growth arose in the noble metals currently supported by the occlusion reduction type catalyst, and there was fault that the purification engine performance fell by reduction in the active spot.
[0005]
Then, NOx which supported noble metals to cerium oxide powder or CeO2-ZrO2 multiple-oxide powder at JP,2001-149757,A The occlusion reduction type catalyst is indicated. Thus, although the noble metals of a reason supported by the support which contains a cerium oxide at least are unknown, the grain growth in hot lean atmosphere is controlled. Therefore, it can consider as the catalyst excellent in endurance.
[0006]
Moreover, NOx It is NOx, in order to raise the activity as a three way component catalyst and to control grain growth of noble metals in the control system of an air-fuel ratio using an occlusion reduction type catalyst, also when an air-fuel ratio is SUTOIKI regularity. It is more desirable that cerium oxide powder or CeO2-ZrO2 multiple oxide is included in an occlusion reduction type catalyst.
[0007]
[Patent reference 1] JP,2001-149757,A
[Patent reference 2] JP,05-168927,A
[0008]
[Problem(s) to be Solved by the Invention]
A cerium oxide is equipped with oxygen occlusion emission ability, under the lean atmosphere of hyperoxia, carries out occlusion of the oxygen and has the property (henceforth OSC ability) of emitting oxygen, under the rich ambient atmosphere where a reduction component is superfluous. Therefore, NOx containing cerium oxide With an occlusion reduction type catalyst, a reduction component is consumed by the oxygen emitted from cerium oxide at the time of a rich spike, and it is NOx. There was fault that purification became difficult. Therefore, NOx Occlusion material is NOx. Where occlusion is carried out, it will be again put to the exhaust gas of the lean atmosphere of hyperoxia, and it is new NOx. Occlusion becomes difficult and it is NOx. The phenomenon of decline in the rate of purification arises.
[0009]
It is made in view of such a situation, a cerium oxide is used efficiently, and this invention is NOx. It aims at preventing decline in the rate of purification.
[0010]
[Means for Solving the Problem]
The description of the catalyst for emission gas purification of this invention which solves the above-mentioned technical problem is noble metals and NOx to oxide support. NOx which comes to support occlusion material In the catalyst for emission gas purification of an occlusion reduction type, oxide support has CeO2 in the Seria system multiple oxide particle of many heterogeneity structures of little [inside] on a front face being included.
[0011]
As for the Seria system multiple oxide, it is desirable that it is CeO2-ZrO2 multiple oxide. Moreover, as for noble metals, it is

desirable to be supported by the Seria system multiple oxide particle particle at least.
[0012]
Furthermore, as for the Seria system multiple oxide particle, being mostly contained in the exhaust gas downstream is more desirable than the exhaust gas upstream.
[0013]
And the description of the emission-gas-purification approach of this invention is NOx which the catalyst for emission gas purification of this invention is contacted to the exhaust gas discharged from the lean-burn engine with which it is operated by 15 or more fuel lean atmosphere, and an air-fuel ratio (A/F) is intermittently made into a SUTOIKI - fuel rich ambient atmosphere, and is contained in exhaust gas. It is NOx at the Lean side. Occlusion is carried out to occlusion material and it is NOx at a rich side from SUTOIKI. NOx emitted from occlusion material It is in returning.
[0014]
As for fuel lean atmosphere, it is still more desirable that an air-fuel ratio (A/F) is 18 or more.
[0015]
[Embodiment of the Invention]
Support containing a cerium oxide It turns out that OSC ability is proportional to the amount of a cerium oxide. However, it became clear by research of this invention person that there is almost no operation of the internal cerium oxide for which the depressant action of grain growth of the noble metals supported by the support containing a cerium oxide was influenced by only the amount of the cerium oxide near [which is supported] the noble metals and which is separated from the noble metals currently supported.
[0016]
So, with the catalyst for emission gas purification of this invention, CeO2 uses the oxide support containing many Seria system multiple oxide particle of little [inside] heterogeneity structure on a front face. Grain growth of noble metals is controlled by considering as such a configuration by CeO2 which exists on a particle front face mostly. and inside a particle, since there is little CeO2, the absolute magnitude of CeO2 decreases conventionally -- since OSC ability becomes lower than before, consumption of the reduction component at the time of a rich spike controls -- having -- this -- NOx Decline in the rate of purification is controlled. In addition, in order to make max discover this operation effectiveness, as for noble metals, it is desirable to be supported by the Seria system multiple oxide particle of heterogeneity structure at least.
[0017]
As for the Seria system multiple oxide particle of heterogeneity structure, being mostly contained in the exhaust gas downstream is more desirable than the exhaust gas upstream. Thus, with constituting, consumption by the oxygen of the reduction component at the time of a rich spike can be controlled in the exhaust gas upstream. Therefore, it is NOx also in the same amount of reducing agents as the former. The rate of purification improves and it is NOx. Since equivalent, then the amount of reducing agents can reduce the rate of purification, fuel consumption improves. That is, it is NOx about a reduction component. It can use for reduction efficiently. And oxidation purification of the excessive reduction component can be carried out by the oxygen emitted since OSC ability was discovered also in the exhaust gas downstream. Therefore, it is NOx about the reduction component introduced by the rich spike. It can use for reduction purification efficiently and is NOx. While the rate of purification improves, discharge of HC and CO is also controlled.
[0018]
As a Seria system multiple oxide particle of heterogeneity structure, although CeO2-ZrO2 multiple oxide, 2OCeO2-aluminum3 multiple oxide, CeO2-TiO2 multiple oxide, CeO2-SiO2 multiple oxide, etc. can be used, especially CeO2-ZrO2 multiple oxide is desirable. Since the stability of CeO2 improves by compound-izing ZrO2 and grain growth of CeO2 the very thing is controlled, grain growth of the noble metals accompanying grain growth of CeO2 can also be controlled. For example, although especially the presentation ratio of CeO2-ZrO2 multiple oxide is not restricted, it is desirable that it is the range of Ce/Zr=5 / 95 - 50/50 in a mole ratio. If control of grain growth of noble metals will become difficult if there is less Ce than this range, and Ce increases more than this range OSC ability becomes high too much and it is NOx. The rate of purification comes to fall.
[0019]
In the Seria system multiple oxide particle of little [inside] heterogeneity structure with much CeO2 on a front face, it is desirable for the amount of cerium elements in a front face especially to be 60% or more that what is necessary is just to exceed 50% of the total amount of cerium elements in the Seria system multiple oxide particle of heterogeneity structure. Control of the grain growth of noble metals by the amount of cerium elements in a front face being 50% or less of the total amount of cerium elements becomes difficult. Moreover, as for the total amount of cerium elements in the Seria system multiple oxide particle, it is desirable that it is less than [50 mol %] to the total amount of metallic elements of the Seria system multiple oxide particle of heterogeneity structure. If the total amount of cerium elements increases more than this range OSC ability becomes high too much and it is NOx. The rate of purification comes to fall.
[0020]
It is ZrO2 powder in order for CeO2 to manufacture many Seria system multiple oxide particles of little [inside] heterogeneity structure on a front face. There is a method of sinking in and calcinating a cerium-nitrate water solution to 2Oaluminum3 powder. Or ZrO2 precursor is deposited from an oxy-zirconium-nitrate water solution, a cerium-nitrate water solution can be mixed after that, CeO2 precursor can be deposited on the front face of ZrO2 precursor, and it can also manufacture by calcinating it. Moreover, it is also possible to make a cerium alkoxide hydrolyze on front faces, such as ZrO2 or ZrO2 precursor, and to calcinate and manufacture it.
[0021]
That what is necessary is just to include the Seria system multiple oxide particle of the above-mentioned heterogeneity structure, the oxide support in the catalyst for emission gas purification of this invention may be constituted only from powder of the Seria system multiple oxide particle of heterogeneity structure, and can also mix other oxide powder. Moreover, the overcoat of the coat layer containing the powder of the Seria system multiple oxide particle of heterogeneity structure can also be carried out to the front face of the coat layer which consists of other oxides. Although aluminum 2O3, ZrO2, TiO2, etc. are illustrated as other oxide powder, when mixing and using the powder of the Seria system multiple oxide particle of heterogeneity structure, and other oxide powder, it is desirable for the powder of the Seria system multiple oxide particle of heterogeneity structure to be made to be contained in oxide support more than 10 volume %.
[0022]
Although chosen from Pt, Rh, Pd, Ir, etc. as noble metals, it is desirable to include Pt with high oxidation activity at least. In addition, the amount of support of the noble metals of the oxide support containing the Seria system multiple oxide particle of heterogeneity structure receives support. It will be expensive, while activity will be saturated even if the purification activity as a catalyst for

emission gas purification is not acquired but it supports exceeding 10 % of the weight if there is less 0.1 - 10 % of the weight than being suitable and 0.1 % of the weight.
[0023]
NOx Occlusion material can be chosen from the rare earth elements except alkali metal, alkaline earth metal, and a cerium, and can be used. It is desirable that it is the metal chosen from alkali metal and alkaline earth metal, and especially the thing for which both alkali metal and alkaline earth metal are supported is desirable. Moreover, NOx The range of 0.01-5 mols per l. of the catalyst for emission gas purification is suitable for the amount of support of occlusion material. It is NOx if fewer than 0.01 mols. If decontamination capacity is too low, is not practical and supports exceeding five mols, the activity of noble metals will come to fall.
[0024]
When considering as the catalyst for emission gas purification containing more Seria system multiple oxide particles to the exhaust gas downstream of heterogeneity structure than the exhaust gas upstream, you may make it the concentration of the Seria system multiple oxide particle increase more than the exhaust gas upstream in the exhaust gas downstream, and it does not contain the Seria system multiple oxide particle in the exhaust gas upstream, but you may make it contain only in the exhaust gas downstream. In addition, it is desirable that the die length from a downstream end face considers as 10 - 70% of range to the overall length of the catalyst for emission gas purification of an exhaust gas flow direction, and, as for the exhaust gas downstream, it is desirable especially to consider as 30 - 50% of range.
[0025]
Moreover, when considering as the catalyst for emission gas purification containing more Seria system multiple oxide particles to the exhaust gas downstream of heterogeneity structure than the exhaust gas upstream, it can mix to oxide support, a coat layer may be formed, and an overcoat can also be carried out to the front face of an oxide support layer.
[0026]
And NOx which the catalyst for emission gas purification of this invention is contacted to the exhaust gas discharged from the lean-burn engine with which it is operated by 15 or more fuel lean atmosphere, and an air-fuel ratio (A/F) is intermittently made into a SUTOIKI - fuel rich ambient atmosphere by the emission-gas-purification approach of this invention, and is contained in exhaust gas It is NOx at the Lean side. Occlusion is carried out to occlusion material and it is NOx at a rich side from SUTOIKI. NOx emitted from occlusion material It returns.
[0027]
In the exhaust gas of a SUTOIKI - fuel rich ambient atmosphere, it is NOx. NOx by which occlusion was carried out to occlusion material It is emitted and is returned by reduction components, such as HC, CO, etc. which exist in an ambient atmosphere. although the Seria system multiple oxide particle of heterogeneity structure is contained in oxide support at this time -- the -- since OSC ability is lower than before, consumption of a reduction component controls -- having -- this -- NOx decline in the rate of purification controls -- having -- high NOx Decontamination capacity is discovered.
[0028]
And consumption by the oxygen of a reduction component can be controlled in the catalyst for emission gas purification containing more Seria system multiple oxide particles to the exhaust gas downstream of heterogeneity structure than the exhaust gas upstream, then the exhaust gas upstream, and it is NOx about a reduction component. It can use for reduction efficiently. Therefore, it is NOx also in the same amount of reducing agents as the former. The rate of purification improves and it is NOx. Since equivalent, then the amount of reducing agents can reduce the rate of purification, fuel consumption improves. And to some extent in the exhaust gas downstream Oxidation purification of the excessive reduction component can be carried out by the oxygen emitted since OSC ability was discovered.
[0029]
[Example]
Hereafter, an example and the example of a comparison explain this invention concretely.
[0030]
(Example 1)
The aqueous ammonia of the amount which serves as Zr:NH 3 = 2:3 by the mole ratio was fed into the water solution of predetermined concentration which dissolved the oxy-zirconium nitrate in distilled water, it agitated at 80 degrees C for 30 minutes, and ZrO2 precursor (zirconium hydroxide) was deposited. Subsequently, in this solution, the cerium-nitrate water solution containing the cerium ion of the amount used as Zr:Ce=9:1 was added and agitated by the mole ratio, and the aqueous ammonia of the amount which serves as Ce:NH 3 = 2:3 by the mole ratio was thrown in, and it agitated at 80 degrees C for 30 minutes. Thereby, CeO2 precursor deposited on the front face by using ZrO2 precursor as a nucleus. this solution is filtered -- it calcinated at the 24-hour desiccation back and 600 degree C by 110 degree C for 5 hours, and CeO2-ZrO2 multiple-oxide powder was prepared.
[0031]
CeO2 (2) distributed and compound-ized by the front face of ZrO2 as a nucleus (1), and ZrO2 (1) as this CeO2-ZrO2 multiple-oxide powder was shown in drawing 1 -- since -- it consists of particles of the becoming heterogeneity structure.
[0032]
a binder (aluminium nitrate) is mixed with this CeO2-ZrO2 multiple-oxide powder and distilled water, a slurry is prepared, and a wash coat is carried out to the 35 cc monolith honeycomb base material made from a ceramic -- it calcinated at the 2-hour desiccation back and 500 degree C by 250 degree C for 2 hours, and the coat layer was formed. A coat layer is per 1l. of monolith honeycomb base materials. 200g was formed.
[0033]
next, the specified quantity of the dinitrodiammine platinum solution of predetermined concentration is infiltrated into the monolith honeycomb base material with which the coat layer was formed -- it calcinated at 500 degree C for 1 hour, and Pt was supported in the coat layer. subsequently, the specified quantity of the water solution which barium acetate and potassium acetate dissolved by predetermined concentration is infiltrated -- it calcinated at 550 degree C for 2 hours, and Ba and K were supported. 2g and Ba the amount of support of each component 0.2 mols and K are 0.15 mols. [per / Pt / 1l. of monolith honeycomb base materials]
[0034]
(Example 2)
Except having added the cerium-nitrate water solution which contains the cerium ion of the amount set to Zr:Ce=7:3 by the mole ratio in the solution with which ZrO2 precursor (zirconium hydroxide) deposited, CeO2-ZrO2 multiple-oxide powder was prepared like the example 1, and the catalyst of an example 2 was prepared like the example 1 except having used the CeO2-ZrO2 multiple-oxide powder.
[0035]

(Example 1 of a comparison)
The aqueous ammonia of the amount which serves as :(Zr+Ce) NH 3 = 2:3 by the mole ratio was fed into the water solution which dissolved the oxy-zirconium nitrate and the cerium nitrate in distilled water so that it might be set to Zr:Ce=9:1 by the mole ratio, and it agitated at 80 degrees C for 30 minutes. this solution is filtered -- 110 degree C -- after 24-hour desiccation It calcinated at 600 degrees C for 5 hours, and the CeO2-ZrO2 multiple-oxide powder which consists of a homogeneous CeO2-ZrO2 multiple-oxide particle from a front face to the interior was prepared.
[0036]
And the catalyst of the example 1 of a comparison was prepared like the example 1 except having used this CeO2-ZrO2 multiple-oxide powder.
[0037]
(Example 2 of a comparison)
Except having used the water solution which dissolved the oxy-zirconium nitrate and the cerium nitrate in distilled water so that it might be set to Zr:Ce=7:3 by the mole ratio, CeO2-ZrO2 multiple-oxide powder was prepared like the example 1 of a comparison, and the catalyst of the example 2 of a comparison was prepared like the example 1 except having used the CeO2-ZrO2 multiple-oxide powder.
[0038]
<A trial and evaluation>
The amount of surface Ce(s) of the CeO2-ZrO2 multiple-oxide powder prepared in the example 1-2 and the example 1-2 of a comparison was measured in XPS. A result is shown in drawing 2 . Drawing 2 to the example 1 has more amounts of surface Ce(s) than the example 1 of a comparison, from the example 2 of a comparison, it is clear that there are many amounts of surface Ce(s), and, as for an example 2, most is considered to have structure as shown in drawing 1 , as for the CeO2-ZrO2 multiple-oxide particle prepared in the example 1-2.
[0039]
Next, saturation NOx of the whole catalyst when circulating the Lean model gas which arranges each catalyst to evaluation equipment, respectively, and is shown in Table 1 The amount of occlusion It measured at each temperature of the range of 250 to 550 degree C, respectively. A result is shown in drawing 3 . Moreover, NOx NOx of the whole catalyst when switching the Rich model gas shown in Table 1 at the catalyst with which the amount of occlusion was saturated to Lean model gas a sink and after that for 3 seconds The amount of occlusion (RSNOx the amount of occlusion) was measured at each temperature, respectively. The total flow is a part for 30L/. A result is shown in drawing 4 .
[0040]
[Table 1]

	H_2 (%)	NO (ppm)	C_3H_6 (ppmC)	CO_2 (%)	CO (%)	O_2 (%)	SO_2 (ppm)	N_2
Leanガス	—	400	2500	9.5	0.1	7.0	—	残部
Richガス	2.0	400	3200	12	6.0	—	—	残部

[0041]
Subsequently, the durability test as for which the Lean model gas shown in Table 2 circulates Rich model gas at 800 degree C by turns by a unit of 5 second for 55 seconds for 4 hours was performed to each catalyst. The total flow is a part for 30L/.
[0042]
[Table 2]

	H_2 (%)	NO (ppm)	C_3H_6 (ppmC)	CO_2 (%)	CO (%)	O_2 (%)	SO_2 (ppm)	N_2
Leanガス	—	800	930	7.3	—	10.5	—	残部
Richガス	0.89	—	2000	11.3	3.59	—	—	残部

[0043]
And it is the saturation NOx of the whole catalyst like [catalyst / after a durability test / each] the above. The amount of occlusion, and RSNOx The amount of occlusion is measured, respectively and a result is shown in drawing 5 and drawing 6 .
[0044]
It is the early saturation NOx from drawing 3 and drawing 4 . If it is equivalent also to each catalyst and the amount of support of Pt (the number of the active spots) is the same, NO will oxidize, and the amount of occlusion is NO2. It becomes and is NOx. It turns out that the amount by which occlusion is carried out to occlusion material is fixed regardless of the amount of Ce(s). moreover, NOx after a rich spike the amount of occlusion (RSNOx the amount of occlusion) -- < (example 1 of an example 1** comparison) (example 2 of an example 2** comparison) -- it is . Namely, the amount in which a reduction component is consumed by the oxygen emitted from CeO2 at the time of a rich spike and NOx which remains without being purified by it An amount is determined by the total amount of Ce(s) in a coat layer, and its unrelated thing is clear to the amount of surface Ce(s).
[0045]
Saturation NOx of a low-temperature-on the other hand region after [drawing 5 and drawing 6 to] a durability test The amount of occlusion is the example of example of comparison 1< example 1< comparison 2< example 2, and is RSNOx of a low-temperature region. The amount of occlusion serves as the example of example of comparison 1< comparison 2< example 1< example 2. That is, if the same amount of Ce(s) compares, the direction of an example 1 and an example 2 is Saturation NOx from the example 1 of a comparison, and the example 2 of a comparison. The amount of occlusion, and RSNOx There are many both amounts of occlusion.

The direction of the catalyst of an example 1 and an example 2 means that the activity of Pt is high, and this means that grain growth of Pt at the time of a durability test has few catalysts of an example 1 and an example 2. That is, with the catalyst of an example 1 and an example 2, since there are many amounts of surface Ce(s) of a CeO2-ZrO2 multiple-oxide particle, it turns out that grain growth of Pt at the time of a durability test was controlled.

[0046]

Therefore, it is clear that the amount in which a reduction component is consume by the oxygen emit from CeO2 at the time of a rich spike can be lessen while being able to control grain growth of Pt at the time of a durability test, if the total amount of Ce(s) is control by lessen the internal amount of Ce(s) while make [many] the amount of surface Ce(s), and the catalyst of this invention is NOx high [excel in endurance]. It is clear that the purification engine performance is discover.

[0047]

(Example 3)

2Oaluminum3 powder 100g and TiO2 powder after mixing 100g, a slurry is prepared, and a wash coat is carried out to the 35 cc monolith honeycomb base material made from a ceramic -- it calcinated at the 2-hour desiccation back and 500 degree C by 250 degree C for 2 hours, and the coat layer was formed. A coat layer is per 1l. of monolith honeycomb base materials. 200g was formed. The specified quantity of the dinitrodiammine platinum solution of predetermined concentration was infiltrated into the monolith honeycomb base material with which this coat layer was formed, it calcinated at 500 degrees C for 1 hour, and Pt was supported in the coat layer. The amount of support of Pt is 2g per 1l. of monolith honeycomb base materials.

[0048]

next, the slurry which contains the CeO2-ZrO2 multiple-oxide powder of heterogeneity structure prepared in the example 1 30% of the weight is prepared, and a wash coat is carried out only to 1/10 of an overall length of the range of die length from the downstream end face of a monolith honeycomb base material with the coat layer which supported Pt -- it calcinated at the 2-hour desiccation back and 500 degree C by 250 degree C for 2 hours, and the overcoat layer was formed. 10g per 1l. of monolith honeycomb base materials of overcoat layers was formed.

[0049]

subsequently, the specified quantity of the water solution which barium acetate and potassium acetate dissolved by predetermined concentration is infiltrated -- it calcinated at 550 degree C for 2 hours, and Ba and K were supported. 2g and Ba the amount of support of each component 0.2 mols and K are 0.15 mols. [per / Pt / 1l. of monolith honeycomb base materials]

[0050]

(Example 4)

It is the same as that of an example 3 except having formed the overcoat layer only in one third of the range of die length of an overall length from the downstream end face. 10g per 1l. of monolith honeycomb base materials of overcoat layers is formed.

[0051]

(Example 5)

It is the same as that of an example 3 except having formed the overcoat layer only in one half of the range of die length of an overall length from the downstream end face. 10g per 1l. of monolith honeycomb base materials of overcoat layers is formed.

[0052]

(Example 6)

It is the same as that of an example 3 except having formed the overcoat layer only in two thirds of the range of die length of an overall length from the downstream end face. 10g per 1l. of monolith honeycomb base materials of overcoat layers is formed.

[0053]

(Example 7)

It is the same as that of an example 3 except having formed the overcoat layer in the overall length. 10g per 1l. of monolith honeycomb base materials of overcoat layers is formed.

[0054]

(Example 3 of a comparison)

An overcoat layer is not formed but they are Ba and K in Pt. It is the same as that of an example 3 except having supported in the coat layer which consists of aluminum 2O3 and TiO2.

[0055]

<A trial and evaluation>

Each catalyst has been arranged to evaluation equipment, respectively, and the durability test as for which the Lean model gas shown in Table 2 circulates Rich model gas at 800 degree C by turns by a unit of 5 second for 55 seconds for 4 hours was performed, respectively. The total flow is a part for 30L/.

[0056]

And NOx when repeating Rich model gas by turns by a unit of 3 second, and circulating the Lean model gas shown in Table 1 for 60 seconds, about each catalyst after a durability test, The rate of purification and HC discharge were measured. Whenever [catalyst floor temperature] It is 300 degrees C. A result is shown in drawing 7 and drawing 8 .

[0057]

The catalyst of each example is compared with the catalyst of the example 3 of a comparison from drawing 7 , and it is high NOx. The rate of purification is shown and it is clear that this it is the effectiveness in which the coat layer which consists of Seria system multiple oxide powder of heterogeneity structure was formed. Moreover, it is clear from the comparison of examples that formation range's of an overcoat layer it is desirable to consider as 10 - 70% of range to an overall length, and it is also desirable especially to consider as 30 - 50% of range.

[0058]

The catalyst of each example shows low HC discharge compared with the catalyst of the example 3 of a comparison, and it is still clearer than drawing 8 that this it is the effectiveness in which the coat layer which consists of Seria system multiple oxide powder of heterogeneity structure was formed. Moreover, it is NOx to what no difference is almost in the discharge of HC although each example of the amount of the Seria system multiple oxide of heterogeneity structure is the same. There is a big difference in the rate of purification. For this, consumed HC is NOx. HC which is because the effectiveness used for reduction differs, is forming an overcoat layer in the exhaust gas downstream like examples 3-6, and is consumed by oxygen is reduced, and the part is NOx. It is thought that it was consumed by reduction and it is thought that the use effectiveness of HC improved.

[0059]

[Effect of the Invention]

That is, since CeO2 is used efficiently and grain growth of noble metals is controlled, while the endurance of the purification engine

performance improves according to the catalyst for emission gas purification and the emission-gas-purification approach of this invention, consumption of the reducibility component at the time of a rich spike is controlled, and it is NOx. Decline in the rate of purification can be prevented.

[Brief Description of the Drawings]

[Drawing 1] It is the explanatory view showing the configuration of the CeO2-ZrO2 multiple-oxide particle of the heterogeneity structure prepared in the one example of this invention.

[Drawing 2] It is the graph which shows the amount of surface Ce(s) of the CeO2-ZrO2 multiple-oxide particle of the heterogeneity structure prepared in the example and the example of a comparison.

[Drawing 3] Saturation NOx in the early stages of the catalyst of an example and the example of a comparison It is the graph which shows the amount of occlusion.

[Drawing 4] RSNOx in the early stages of the catalyst of an example and the example of a comparison It is the graph which shows the amount of occlusion.

[Drawing 5] Saturation NOx after the durability test of the catalyst of an example and the example of a comparison It is the graph which shows the amount of occlusion.

[Drawing 6] RSNOx after the durability test of the catalyst of an example and the example of a comparison It is the graph which shows the amount of occlusion.

[Drawing 7] NOx after the durability test of the catalyst of an example and the example of a comparison It is the graph which shows the rate of purification.

[Drawing 8] It is the graph which shows HC discharge after the durability test of the catalyst of an example and the example of a comparison.

[Description of Notations]

1:ZrO2 2:CeO2

[Translation done.]

* NOTICES *

JPO and NCIPI are not responsible for any
damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the explanatory view showing the configuration of the CeO2-ZrO2 multiple-oxide particle of the heterogeneity structure prepared in the one example of this invention.
[Drawing 2] It is the graph which shows the amount of surface Ce(s) of the CeO2-ZrO2 multiple-oxide particle of the heterogeneity structure prepared in the example and the example of a comparison.
[Drawing 3] Saturation NOx in the early stages of the catalyst of an example and the example of a comparison It is the graph which shows the amount of occlusion.
[Drawing 4] RSNOx in the early stages of the catalyst of an example and the example of a comparison It is the graph which shows the amount of occlusion.
[Drawing 5] Saturation NOx after the durability test of the catalyst of an example and the example of a comparison It is the graph which shows the amount of occlusion.
[Drawing 6] RSNOx after the durability test of the catalyst of an example and the example of a comparison It is the graph which shows the amount of occlusion.
[Drawing 7] NOx after the durability test of the catalyst of an example and the example of a comparison It is the graph which shows the rate of purification.
[Drawing 8] It is the graph which shows HC discharge after the durability test of the catalyst of an example and the example of a comparison.
[Description of Notations]
1:ZrO2 2:CeO2

[Translation done.]

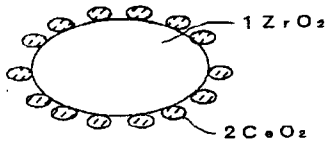
* NOTICES *

JPO and NCIPI are not responsible for any
damages caused by the use of this translation.

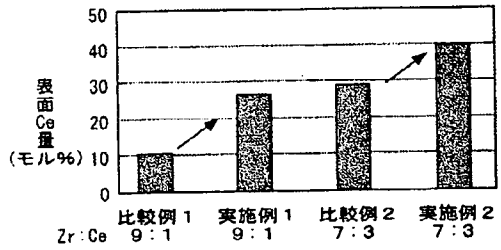
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

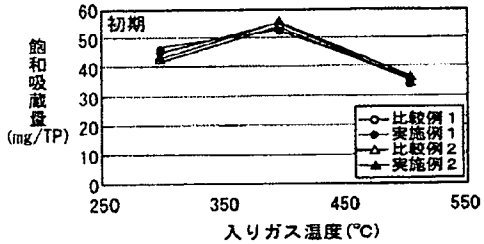
[Drawing 1]



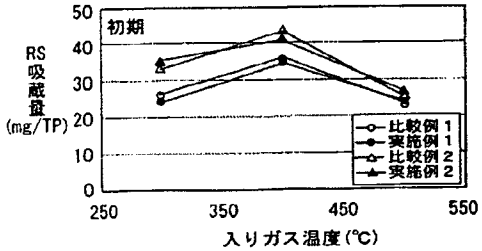
[Drawing 2]



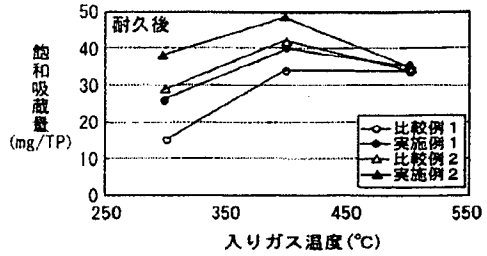
[Drawing 3]



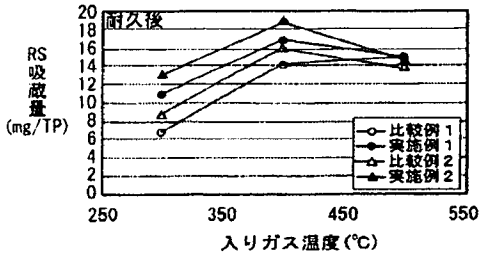
[Drawing 4]



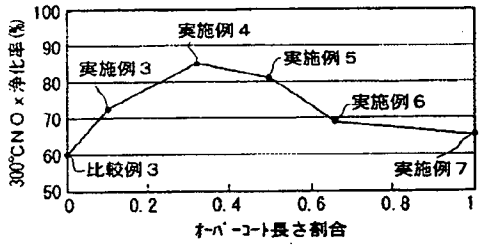
[Drawing 5]



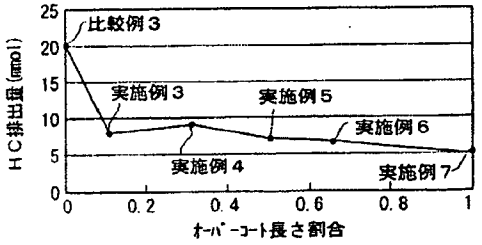
[Drawing 6]



[Drawing 7]



[Drawing 8]



[Translation done.]

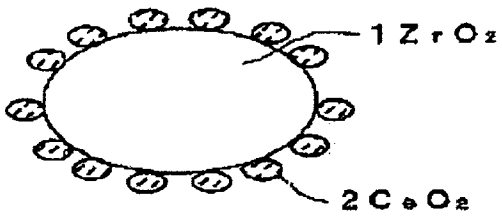
CATALYST FOR EXHAUST GAS PURIFICATION, AND EXHAUST GAS PURIFICATION METHOD

Publication number: JP2004074138
Publication date: 2004-03-11
Inventor: HARA NAOYUKI
Applicant: TOYOTA MOTOR CORP
Classification:
- international: ***F01N3/10; B01D53/94; B01J23/58; F01N3/20; F02D41/04;*** **F01N3/10; B01D53/94; B01J23/54; F01N3/20; F02D41/04;** (IPC1-7): B01J23/58; B01D53/94; F01N3/10; F01N3/20; F02D41/04
- european:
Application number: JP20020285223 20020930
Priority number(s): JP20020285223 20020930; JP20020175830 20020617

Report a data error here

Abstract of **JP2004074138**

PROBLEM TO BE SOLVED: To suppress the granular growth of noble metals using cerium oxide and to prevent lowering of NOx purification rate.
SOLUTION: A noble metal is carried on an oxide carrier containing cerium-based compound oxide particles of an ununiform constitution having a large amount of CeO<SB>2</SB>on the surface and less in the inner part. The granular growth the noble metal is suppressed by CeO<SB>2</SB>much existing on the surface. The absolute amount of CeO<SB>2</SB>is less than that in the conventional case, as the content of CeO<SB>2</SB>in the inner part is small, causing less capacity of oxygen storing and releasing. This suppresses the consumption of a reducing component in rich spiking, to suppress the lowering of the NOx purification rate.
COPYRIGHT: (C)2004,JPO



Data supplied from the ***esp@cenet*** database - Worldwide

(19)日本国特許庁(JP)　(12)公開特許公報(A)　(11)特許出願公開番号
特開2004-74138
(P2004-74138A)
(43)公開日　平成16年3月11日(2004.3.11)

(51)Int.Cl.[7]		F I			テーマコード（参考）
B01J 23/58		B01J	23/58	ZABA	3G091
B01D 53/94		F01N	3/10	A	3G301
F01N 3/10		F01N	3/20	R	4D048
F01N 3/20		F02D	41/04	305A	4G069
F02D 41/04		B01D	53/36	104A	

審査請求 未請求　請求項の数 6　OL　（全 12 頁）　最終頁に続く

(21)出願番号　特願2002-285223(P2002-285223)
(22)出願日　平成14年9月30日(2002.9.30)
(31)優先権主張番号　特願2002-175830(P2002-175830)
(32)優先日　平成14年6月17日(2002.6.17)
(33)優先権主張国　日本国(JP)

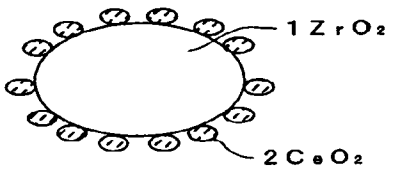
(71)出願人　000003207
トヨタ自動車株式会社
愛知県豊田市トヨタ町１番地
(74)代理人　100081776
弁理士　大川　宏
(72)発明者　原　尚之
愛知県豊田市トヨタ町１番地　トヨタ自動車株式会社内

Fターム(参考)　3G091 AA12 AB05 AB06 BA14 BA39 GA06 GB02Y GB03Y GB04W GB04Y GB05W GB17X
3G301 HA15 JA21 JA25 LB04 MA01 NE13 NE14

最終頁に続く

(54)【発明の名称】排ガス浄化用触媒及び排ガス浄化方法

(57)【要約】
【課題】セリウム酸化物を用いて貴金属の粒成長を抑制するとともに、NO_x　浄化率の低下を防止する。
【解決手段】CeO_2が表面に多く内部に少ない不均質構造のセリア系複合酸化物粒子を含む酸化物担体に貴金属を担持した。
表面に多く存在するCeO_2によって貴金属の粒成長が抑制される。そして内部にはCeO_2が少ないのでCeO_2の絶対量が従来より少なくなり、酸素吸蔵放出能が従来より低くなるため、リッチスパイク時における還元成分の消費が抑制され、これによってNO_x　浄化率の低下が抑制される。
【選択図】　図１



【特許請求の範囲】
【請求項１】
酸化物担体に貴金属とＮＯｘ 吸蔵材とを担持してなるＮＯｘ 吸蔵還元型の排ガス浄化用触媒において、
該酸化物担体は、CeO_2が表面に多く内部に少ない不均質構造のセリア系複合酸化物粒子を含むことを特徴とする排ガス浄化用触媒。
【請求項２】
前記セリア系複合酸化物はCeO_2－ＺｒＯ２複合酸化物である請求項１に記載の排ガス浄化用触媒。
【請求項３】
前記貴金属は少なくとも前記セリア系複合酸化物粒子に担持されている請求項１に記載の排ガス浄化用触媒。
【請求項４】
前記セリア系複合酸化物粒子は排ガス上流側より排ガス下流側に多く含まれている請求項１に記載の排ガス浄化用触媒。
【請求項５】
請求項１～４のいずれかに記載の排ガス浄化用触媒を、空燃比（Ａ／Ｆ）が１５以上の燃料リーン雰囲気で運転され間欠的にストイキ～燃料リッチ雰囲気とされる希薄燃焼エンジンから排出される排ガスと接触させ、該排ガス中に含まれるＮＯｘ をリーン側で該ＮＯｘ 吸蔵材に吸蔵し、ストイキからリッチ側で該ＮＯｘ 吸蔵材から放出されたＮＯｘ を還元することを特徴とする排ガス浄化方法。
【請求項６】
前記燃料リーン雰囲気は空燃比（Ａ／Ｆ）が１８以上である請求項５に記載の排ガス浄化方法。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】
本発明は、酸素過剰のリーン雰囲気と還元成分過剰のリッチ雰囲気とが交互に切り替えられる排ガス中で使用されるＮＯｘ 吸蔵還元型の排ガス浄化用触媒と、その排ガス浄化用触媒を用いた排ガス浄化方法に関する。
【０００２】
【従来の技術】
燃費の向上とともに二酸化炭素の排出の抑制を目的とし、近年の自動車には酸素過剰のリーン雰囲気で燃焼されるリーンバーンエンジンが用いられている。ところがリーンバーンエンジンからの排ガスは酸素過剰のリーン雰囲気であるために、一般の三元触媒では、ＨＣ，ＣＯの浄化は可能であるもののＮＯｘ の還元浄化が困難である。
【０００３】
そこで酸化物担体に貴金属とＮＯｘ 吸蔵材とを担持してなるＮＯｘ 吸蔵還元型触媒が開発され、空気過剰のリーン雰囲気と燃料過剰のリッチ雰囲気とを交互に切り替える燃焼条件下にて用いられている。空気過剰のリーン雰囲気での燃焼排ガスは酸素過剰のリーン雰囲気であるので、排ガス中のＮＯは酸化によってNO_2となりＮＯｘ 吸蔵材に硝酸塩などとして吸蔵される。そして燃料過剰のリッチ雰囲気の燃焼排ガスは還元成分過剰のリッチ雰囲気であり、その雰囲気下では吸蔵されていたＮＯｘ がＮＯｘ 吸蔵材から放出され雰囲気中に豊富に存在する還元成分によってN_2まで還元され浄化される。
【０００４】
そして燃費の向上及び二酸化炭素の排出抑制の目的を達成するためには、空気過剰のリーン雰囲気での燃焼時間を長くし、燃料過剰のリッチ雰囲気での燃焼時間は短くする必要があり、常時はリーン雰囲気で燃焼させ燃料過剰のリッチ雰囲気をパルス的に導入する（リッチスパイク）ことが行われている。しかし空気過剰のリーン雰囲気での燃焼排ガスは、高温の酸化性雰囲気であるために、ＮＯｘ 吸蔵還元型触媒に担持されている貴金属に粒

成長が生じ、活性点の減少によって浄化性能が低下するという不具合があった。

【０００５】

そこで特開２００１－１４９７５７号公報には、セリウム酸化物粉末又はCeO_2－ジルコニア(ZrO_2)複合酸化物粉末に貴金属を担持したNO_x吸蔵還元型触媒が開示されている。このように少なくともセリウム酸化物を含む担体に担持された貴金属は、理由は不明であるが、高温のリーン雰囲気における粒成長が抑制される。したがって耐久性に優れた触媒とすることができる。

【０００６】

またNO_x吸蔵還元型触媒を用いた空燃比の制御システムにおいて、空燃比がストイキ一定の場合にも、三元触媒としての活性を向上させ、かつ貴金属の粒成長を抑制するために、NO_x吸蔵還元型触媒にセリウム酸化物粉末又はCeO_2－ジルコニア(ZrO_2)複合酸化物を含むことがより好ましい。

【０００７】

【特許文献１】特開２００１－１４９７５７号

【特許文献２】特開平０５－１６８９２７号

【０００８】

【発明が解決しようとする課題】

セリウム酸化物は酸素吸蔵放出能を備え、酸素過剰のリーン雰囲気下では酸素を吸蔵し、還元成分過剰のリッチ雰囲気下では酸素を放出するという特性（以下ＯＳＣ能という）を有している。そのためセリウム酸化物を含むNO_x吸蔵還元型触媒では、リッチスパイク時にセリウム酸化物から放出された酸素によって還元成分が消費され、NO_xの浄化が困難になるという不具合があった。そのためNO_x吸蔵材は、NO_xが吸蔵された状態で再び酸素過剰のリーン雰囲気の排ガスに曝されることとなり、新たなNO_xの吸蔵が困難となってNO_x浄化率の低下という現象が生じる。

【０００９】

本発明はこのような事情に鑑みてなされたものであり、セリウム酸化物を効率的に用いてNO_x浄化率の低下を防止することを目的とする。

【００１０】

【課題を解決するための手段】

上記課題を解決する本発明の排ガス浄化用触媒の特徴は、酸化物担体に貴金属とNO_x吸蔵材とを担持してなるNO_x吸蔵還元型の排ガス浄化用触媒において、酸化物担体は、CeO_2が表面に多く内部に少ない不均質構造のセリア系複合酸化物粒子を含むことにある。

【００１１】

セリア系複合酸化物はCeO_2－ジルコニア(ZrO_2)複合酸化物であることが望ましい。また、貴金属は少なくともセリア系複合酸化物粒子粒子に担持されていることが望ましい。

【００１２】

さらに、セリア系複合酸化物粒子は排ガス上流側より排ガス下流側に多く含まれていることが望ましい。

【００１３】

そして本発明の排ガス浄化方法の特徴は、本発明の排ガス浄化用触媒を、空燃比（Ａ／Ｆ）が１５以上の燃料リーン雰囲気で運転され間欠的にストイキ～燃料リッチ雰囲気とされる希薄燃焼エンジンから排出される排ガスと接触させ、排ガス中に含まれるNO_xをリーン側でNO_x吸蔵材に吸蔵し、ストイキからリッチ側でNO_x吸蔵材から放出されたNO_xを還元することにある。

【００１４】

燃料リーン雰囲気は空燃比（Ａ／Ｆ）が１８以上であることがさらに好ましい。

【００１５】

【発明の実施の形態】

セリウム酸化物を含む担体のＯＳＣ能は、セリウム酸化物の量に比例することがわかっ

ている。しかしセリウム酸化物を含む担体に担持された貴金属の粒成長の抑制作用は、担持されている貴金属近傍のセリウム酸化物の量にのみ影響され、担持されている貴金属から離れた内部のセリウム酸化物の作用はほとんどないことが、本発明者の研究により明らかとなった。

【００１６】

そこで本発明の排ガス浄化用触媒では、CeO_2が表面に多く内部に少ない不均質構造のセリア系複合酸化物粒子を含む酸化物担体を用いている。このような構成とすることにより、粒子表面に多く存在するCeO_2によって貴金属の粒成長が抑制される。そして粒子内部にはCeO_2が少ないのでCeO_2の絶対量が従来より少なくなり、ＯＳＣ能が従来より低くなるため、リッチスパイク時における還元成分の消費が抑制され、これによってNO_x浄化率の低下が抑制される。なお、この作用効果を最大に発現させるには、貴金属は少なくとも不均質構造のセリア系複合酸化物粒子に担持されていることが望ましい。

【００１７】

不均質構造のセリア系複合酸化物粒子は、排ガス上流側より排ガス下流側に多く含まれていることが望ましい。このように構成することで、排ガス上流側においては、リッチスパイク時の還元成分の酸素による消費を抑制することができる。したがって従来と同じ還元剤量でもNO_x浄化率が向上し、NO_x浄化率を同等とすれば還元剤量が低減できるので燃費が向上する。すなわち、還元成分をNO_xの還元に効率よく利用することができる。そして排ガス下流側においては、ＯＳＣ能が発現されるため放出された酸素によって余剰の還元成分を酸化浄化することができる。したがってリッチスパイクにより導入された還元成分をNO_xの還元浄化に効率よく利用することができ、NO_x浄化率が向上するとともにＨＣ及びＣＯの排出も抑制される。

【００１８】

不均質構造のセリア系複合酸化物粒子としては、CeO_2－ＺｒO$_2$複合酸化物，CeO_2－Al_2O_3複合酸化物，CeO_2－TiO_2複合酸化物，CeO_2－SiO_2複合酸化物などを用いることができるが、CeO_2－ＺｒO$_2$複合酸化物が特に好ましい。ＺｒO$_2$を複合化することでCeO_2の安定性が向上し、CeO_2自体の粒成長が抑制されるので、CeO_2の粒成長に伴う貴金属の粒成長も抑制することができる。例えばCeO_2－ＺｒO$_2$複合酸化物の組成比は特に制限されないが、モル比でＣｅ／Ｚｒ＝５／９５～５０／５０の範囲であるのが好ましい。Ｃｅがこの範囲より少ないと貴金属の粒成長の抑制が困難となり、Ｃｅがこの範囲より多くなるとＯＳＣ能が高くなりすぎてNO_x浄化率が低下するようになる。

【００１９】

CeO_2が表面に多く内部に少ない不均質構造のセリア系複合酸化物粒子において、表面におけるセリウム元素量は不均質構造のセリア系複合酸化物粒子中の全セリウム元素量の５０％を超えればよく、６０％以上であることが特に望ましい。表面におけるセリウム元素量が全セリウム元素量の５０％以下であると、貴金属の粒成長の抑制が困難となる。またセリア系複合酸化物粒子中の全セリウム元素量は、不均質構造のセリア系複合酸化物粒子の全金属元素量に対して５０モル％以下であることが望ましい。全セリウム元素量がこの範囲より多くなるとＯＳＣ能が高くなりすぎ、NO_x浄化率が低下するようになる。

【００２０】

CeO_2が表面に多く内部に少ない不均質構造のセリア系複合酸化物粒子を製造するには、例えばＺｒO$_2$粉末やAl_2O_3粉末に硝酸セリウム水溶液を含浸して焼成する方法がある。あるいはオキシ硝酸ジルコニウム水溶液からＺｒO$_2$前駆体を析出させ、その後に硝酸セリウム水溶液を混合してＺｒO$_2$前駆体の表面にCeO_2前駆体を析出させ、それを焼成することで製造することもできる。またＺｒO$_2$あるいはＺｒO$_2$前駆体などの表面でセリウムアルコキシドを加水分解させ、それを焼成して製造することも可能である。

【００２１】
本発明の排ガス浄化用触媒における酸化物担体は、上記した不均質構造のセリア系複合酸化物粒子を含めばよく、不均質構造のセリア系複合酸化物粒子の粉末のみから構成してもよいし他の酸化物粉末を混合することもできる。また他の酸化物よりなるコート層の表面に不均質構造のセリア系複合酸化物粒子の粉末を含むコート層をオーバーコートすることもできる。他の酸化物粉末としては、Al_2O_3．ジルコニア．TiO_2などが例示されるが、不均質構造のセリア系複合酸化物粒子の粉末と他の酸化物粉末を混合して用いる場合は、酸化物担体中に不均質構造のセリア系複合酸化物粒子の粉末が１０体積％以上含まれるようにすることが望ましい。

【００２２】
貴金属としてはＰｔ．Ｒｈ．Ｐｄ．Ｉｒなどから選択されるが、酸化活性の高いＰｔを少なくとも含むことが望ましい。なお不均質構造のセリア系複合酸化物粒子を含む酸化物担体の貴金属の担持量は担体に対して　０．１～１０重量％が適当であり、　０．１重量％より少ないと排ガス浄化用触媒としての浄化活性が得られず、１０重量％を超えて担持しても活性が飽和するとともに高価となってしまう。

【００２３】
NO_x　吸蔵材は、アルカリ金属．アルカリ土類金属．セリウムを除く希土類元素の中から選択して用いることができる。アルカリ金属及びアルカリ土類金属の中から選ばれる金属であることが好ましく、アルカリ金属とアルカリ土類金属の両方を担持することが特に望ましい。またNO_x　吸蔵材の担持量は、排ガス浄化用触媒の１リットル当たり０．０１～５モルの範囲が適当である。０．０１モルより少ないとNO_x　浄化能が低すぎて実用的でなく、５モルを超えて担持すると貴金属の活性が低下するようになる。

【００２４】
不均質構造のセリア系複合酸化物粒子を排ガス上流側より排ガス下流側に多く含む排ガス浄化用触媒とする場合、セリア系複合酸化物粒子の濃度が排ガス上流側より排ガス下流側に多くなるようにしてもよいし、セリア系複合酸化物粒子を排ガス上流側に含まず排ガス下流側にのみ含むようにしてもよい。なお排ガス下流側とは、下流側端面からの長さが排ガス流れ方向の排ガス浄化用触媒の全長に対して１０～７０％の範囲とするのが好ましく、３０～５０％の範囲とするのが特に好ましい。

【００２５】
また不均質構造のセリア系複合酸化物粒子を排ガス上流側より排ガス下流側に多く含む排ガス浄化用触媒とする場合、酸化物担体に混合してコート層を形成してもよいし、酸化物担体層の表面にオーバーコートすることもできる。

【００２６】
そして本発明の排ガス浄化方法では、本発明の排ガス浄化用触媒を、空燃比（Ａ／Ｆ）が１５以上の燃料リーン雰囲気で運転され間欠的にストイキ～燃料リッチ雰囲気とされる希薄燃焼エンジンから排出される排ガスと接触させ、排ガス中に含まれるNO_x　をリーン側でNO_x　吸蔵材に吸蔵し、ストイキからリッチ側でNO_x　吸蔵材から放出されたNO_x　を還元する。

【００２７】
ストイキ～燃料リッチ雰囲気の排ガス中では、NO_x　吸蔵材に吸蔵されていたNO_x　が放出され、雰囲気中に存在するＨＣ及びＣＯなどの還元成分によって還元される。このとき酸化物担体には不均質構造のセリア系複合酸化物粒子が含まれているが、その　ＯＳＣ能は従来より低いため還元成分の消費が抑制され、これによってNO_x　浄化率の低下が抑制され高いNO_x　浄化能が発現される。

【００２８】
そして不均質構造のセリア系複合酸化物粒子を排ガス上流側より排ガス下流側に多く含む排ガス浄化用触媒とすれば、排ガス上流側においては還元成分の酸素による消費を抑制することができ、還元成分をNO_x　の還元に効率よく利用することができる。したがって従来と同じ還元剤量でもNO_x　浄化率が向上し、NO_x　浄化率を同等とすれば還元剤

量が低減できるので燃費が向上する。そして排ガス下流側においては、ある程度のＯＳＣ能が発現されるため放出された酸素によって余剰の還元成分を酸化浄化することができる。

【００２９】

【実施例】

以下、実施例及び比較例により本発明を具体的に説明する。

【００３０】

（実施例１）

オキシ硝酸ジルコニウムを蒸留水に溶解した所定濃度の水溶液に、モル比でＺｒ：NH_3＝２：３となる量のアンモニア水を投入し、８０℃で３０分撹　してＺｒO_2前駆体（水酸化ジルコニウム）を析出させた。次いでこの溶液に、モル比でＺｒ：Ｃｅ＝９：１となる量のセリウムイオンを含む硝酸セリウム水溶液を添加して撹　し、モル比でＣｅ：NH_3　＝２：３となる量のアンモニア水を投入して８０℃で３０分撹　した。これによりＺｒO_2前駆体を核として、その表面にＣｅO_2前駆体が析出した。この溶液を　過し、　１１０℃で２４時間乾燥後、　６００℃で５時間焼成してＣｅO_2－ＺｒO_2複合酸化物粉末を調製した。

【００３１】

このＣｅO_2－ＺｒO_2複合酸化物粉末は、図１に示すように、核としてのＺｒO_2（１）と、ＺｒO_2（１）の表面に分散して複合化されたＣｅO_2（２）と、からなる不均質構造の粒子から構成されている。

【００３２】

このＣｅO_2－ＺｒO_2複合酸化物粉末と、蒸留水と、バインダ（硝酸アルミニウム）を混合してスラリーを調製し、３５ｃｃのセラミック製モノリスハニカム基材にウオッシュコートして、　２５０℃で２時間乾燥後、　５００℃で２時間焼成しコート層を形成した。コート層は、モノリスハニカム基材１リットルあたり　２００ｇ形成された。

【００３３】

次に、コート層が形成されたモノリスハニカム基材に、所定濃度のジニトロジアンミン白金水溶液の所定量を含浸させ、　５００℃で１時間焼成してコート層にＰｔを担持した。次いで酢酸バリウムと酢酸カリウムが所定濃度で溶解した水溶液の所定量を含浸させ、５５０℃で２時間焼成してＢａとＫを担持した。各成分の担持量は、モノリスハニカム基材１リットルあたりＰｔが２ｇ、Ｂａが　０．２モル、Ｋが０．１５モルである。

【００３４】

（実施例２）

ＺｒO_2前駆体（水酸化ジルコニウム）が析出した溶液に、モル比でＺｒ：Ｃｅ＝７：３となる量のセリウムイオンを含む硝酸セリウム水溶液を添加したこと以外は実施例１と同様にしてＣｅO_2－ＺｒO_2複合酸化物粉末を調製し、そのＣｅO_2－ＺｒO_2複合酸化物粉末を用いたこと以外は実施例１と同様にして、実施例２の触媒を調製した。

【００３５】

（比較例１）

オキシ硝酸ジルコニウムと硝酸セリウムを、モル比でＺｒ：Ｃｅ＝９：１となるように蒸留水に溶解した水溶液に、モル比で（Ｚｒ＋Ｃｅ）：NH_3　＝２：３となる量のアンモニア水を投入して８０℃で３０分撹　した。この溶液を　過し、　１１０℃で２４時間乾燥後　６００℃で５時間焼成して、表面から内部まで均質なＣｅO_2－ＺｒO_2複合酸化物粒子からなるＣｅO_2－ＺｒO_2複合酸化物粉末を調製した。

【００３６】

そしてこのＣｅO_2－ＺｒO_2複合酸化物粉末を用いたこと以外は実施例１と同様にして、比較例１の触媒を調製した。

【００３７】

（比較例２）

オキシ硝酸ジルコニウムと硝酸セリウムをモル比でＺｒ：Ｃｅ＝７：３となるように蒸留

水に溶解した水溶液を用いたこと以外は比較例１と同様にしてCeO_2－ZrO_2複合酸化物粉末を調製し、そのCeO_2－ZrO_2複合酸化物粉末を用いたこと以外は実施例１と同様にして、比較例２の触媒を調製した。

【００３８】

＜試験・評価＞

実施例１－２及び比較例１－２で調製されたCeO_2－ZrO_2複合酸化物粉末の表面Ｃｅ量をＸＰＳにて測定した。結果を図２に示す。図２から、実施例１は比較例１より表面Ｃｅ量が多く、実施例２は比較例２より表面Ｃｅ量が多いことが明らかであり、実施例１－２で調製されたCeO_2－ZrO_2複合酸化物粒子は大部分が図１に示すような構造になっていると考えられる。

【００３９】

次に、各触媒を評価装置にそれぞれ配置し、表１に示すＬｅａｎモデルガスを流通させたときの触媒全体の飽和NO_x吸蔵量を２５０～５５０℃の範囲の各温度でそれぞれ測定した。結果を図３に示す。またNO_x吸蔵量が飽和した触媒に表１に示すＲｉｃｈモデルガスを３秒間流し、その後Ｌｅａｎモデルガスに切り換えた時の触媒全体のNO_x吸蔵量（$RSNO_x$吸蔵量）を各温度でそれぞれ測定した。総流量は３０Ｌ／分である。結果を図４に示す。

【００４０】

【表１】

	H_2 (%)	NO (ppm)	C_3H_6 (ppmC)	CO_2 (%)	CO (%)	O_2 (%)	SO_2 (ppm)	N_2
Leanガス	—	400	2500	9.5	0.1	7.0	—	残部
Richガス	2.0	400	3200	12	6.0	—	—	残部

【００４１】

次いで各触媒に対して、表２に示すＬｅａｎモデルガスを５５秒，Ｒｉｃｈモデルガスを５秒ずつ交互に、８００℃で４時間流通させる耐久試験を行った。総流量は３０Ｌ／分である。

【００４２】

【表２】

	H_2 (%)	NO (ppm)	C_3H_6 (ppmC)	CO_2 (%)	CO (%)	O_2 (%)	SO_2 (ppm)	N_2
Leanガス	—	800	930	7.3	—	10.5	—	残部
Richガス	0.89	—	2000	11.3	3.59	—	—	残部

【００４３】

そして耐久試験後の各触媒について、上記と同様にして触媒全体の飽和NO_x吸蔵量と$RSNO_x$吸蔵量をそれぞれ測定し、結果を図５及び図６に示す。

【００４４】

図３，図４より、初期の飽和NO_x吸蔵量は各触媒とも同等であり、Ｐｔの担持量（活性点数）が同一であればＮＯが酸化されNO_2となってNO_x吸蔵材に吸蔵される量は、Ｃｅ量に無関係に一定であることがわかる。またリッチスパイク後のNO_x吸蔵量（$RSNO_x$吸蔵量）は、（実施例１≒比較例１）＜（実施例２≒比較例２）である。すなわちリッチスパイク時にCeO_2から放出される酸素によって還元成分が消費される量、及びそれによって浄化されずに残るNO_x量はコート層中の総Ｃｅ量によって決定され、表面Ｃｅ量には無関係であることが明らかである。

【００４５】

一方、図５，図６から、耐久試験後における低温域の飽和NO_x吸蔵量は、比較例１＜

実施例１＜比較例２＜実施例２であり、低温域のＲＳＮＯ$_x$　吸蔵量は比較例１＜比較例２＜実施例１＜実施例２となっている。すなわち同じＣｅ量で比較すると、実施例１及び実施例２の方が比較例１及び比較例２より飽和ＮＯ$_x$　吸蔵量及びＲＳＮＯ$_x$　吸蔵量が共に多い。このことは、実施例１及び実施例２の触媒の方がＰｔの活性が高いことを意味し、実施例１及び実施例２の触媒の方が耐久試験時のＰｔの粒成長が少ないことを意味している。すなわち実施例１及び実施例２の触媒では、CeO_2－ＺｒＯ$_2$複合酸化物粒子の表面Ｃｅ量が多いため、耐久試験時のＰｔの粒成長が抑制されたことがわかる。

【００４６】

したがって、表面Ｃｅ量を多くするとともに内部のＣｅ量を少なくすることで総Ｃｅ量を抑制すれば、耐久試験時のＰｔの粒成長を抑制できるとともに、リッチスパイク時にCeO_2から放出される酸素によって還元成分が消費される量を少なくすることができることが明らかであり、本発明の触媒は耐久性に優れかつ高いＮＯ$_x$　浄化性能が発現されることが明らかである。

【００４７】

（実施例３）

Al_2O_3粉末　１００ｇとTiO_2粉末　１００ｇを混合した後スラリーを調製し、３５ｃｃのセラミック製モノリスハニカム基材にウオッシュコートして、２５０℃で２時間乾燥後、５００℃で２時間焼成しコート層を形成した。コート層は、モノリスハニカム基材１リットルあたり　２００ｇ形成された。このコート層が形成されたモノリスハニカム基材に、所定濃度のジニトロジアンミン白金水溶液の所定量を含浸させ、５００℃で１時間焼成してコート層にＰｔを担持した。Ｐｔの担持量はモノリスハニカム基材１リットルあたり２ｇである。

【００４８】

次に、実施例１で調製された不均質構造のCeO_2－ＺｒＯ$_2$複合酸化物粉末を３０重量％含むスラリーを調製し、Ｐｔを担持したコート層をもつモノリスハニカム基材の下流側端面から全長の１／１０の長さの範囲のみにウォッシュコートして、２５０℃で２時間乾燥後、５００℃で２時間焼成しオーバーコート層を形成した。オーバーコート層は、モノリスハニカム基材１リットルあたり１０ｇ形成された。

【００４９】

次いで酢酸バリウムと酢酸カリウムが所定濃度で溶解した水溶液の所定量を含浸させ、５５０℃で２時間焼成してＢａとＫを担持した。各成分の担持量は、モノリスハニカム基材１リットルあたりＰｔが２ｇ、Ｂａが　０．２モル、Ｋが０．１５モルである。

【００５０】

（実施例４）

オーバーコート層を下流側端面から全長の１／３の長さの範囲のみに形成したこと以外は実施例３と同様である。オーバーコート層は、モノリスハニカム基材１リットルあたり１０ｇ形成されている。

【００５１】

（実施例５）

オーバーコート層を下流側端面から全長の１／２の長さの範囲のみに形成したこと以外は実施例３と同様である。オーバーコート層は、モノリスハニカム基材１リットルあたり１０ｇ形成されている。

【００５２】

（実施例６）

オーバーコート層を下流側端面から全長の２／３の長さの範囲のみに形成したこと以外は実施例３と同様である。オーバーコート層は、モノリスハニカム基材１リットルあたり１０ｇ形成されている。

【００５３】

（実施例７）

オーバーコート層を全長に形成したこと以外は実施例３と同様である。オーバーコート層

は、モノリスハニカム基材１リットルあたり１０ｇ形成されている。

【００５４】

（比較例３）

オーバーコート層を形成せず、ＰｔとともにＢａ及びＫを Al_2O_3 及び TiO_2 からなるコート層に担持したこと以外は実施例３と同様である。

【００５５】

＜試験・評価＞

各触媒を評価装置にそれぞれ配置し、表２に示したＬｅａｎモデルガスを５５秒、Ｒｉｃｈモデルガスを５秒ずつ交互に、８００℃で４時間流通させる耐久試験をそれぞれ行った。総流量は３０Ｌ／分である。

【００５６】

そして耐久試験後の各触媒について、表１に示したＬｅａｎモデルガスを６０秒、Ｒｉｃｈモデルガスを３秒ずつ交互に繰り返し流通させたときの NO_x 浄化率及びＨＣ排出量を測定した。触媒床温度は３００℃である。結果を図７及び図８に示す。

【００５７】

図７より各実施例の触媒は比較例３の触媒に比べて高い NO_x 浄化率を示し、これは不均質構造のセリア系複合酸化物粉末からなるコート層を形成した効果であることが明らかである。また実施例どうしの比較から、オーバーコート層の形成範囲は、全長に対して１０～７０％の範囲とするのが好ましく、３０～５０％の範囲とするのが特に好ましいことも明らかである。

【００５８】

さらに図８より、各実施例の触媒は比較例３の触媒に比べて低いＨＣ排出量を示し、これは不均質構造のセリア系複合酸化物粉末からなるコート層を形成した効果であることが明らかである。また各実施例ともに不均質構造のセリア系複合酸化物の量は同一であるが、ＨＣの排出量にはほとんど差が無いのに NO_x 浄化率には大きな差がある。これは消費されたＨＣが NO_x の還元に利用された効率が異なるためであり、実施例３～６のように排ガス下流側にオーバーコート層を形成することで、酸素によって消費されるＨＣが低減されその分が NO_x の還元に消費されたと考えられ、ＨＣの利用効率が向上したと考えられる。

【００５９】

【発明の効果】

すなわち本発明の排ガス浄化用触媒及び排ガス浄化方法によれば、CeO_2 が効率的に利用されて貴金属の粒成長が抑制されているので浄化性能の耐久性が向上するとともに、リッチスパイク時の還元性成分の消費が抑制され NO_x 浄化率の低下を防止することができる。

【図面の簡単な説明】

【図１】本発明の一実施例で調製された不均質構造の CeO_2－ZrO_2 複合酸化物粒子の構成を示す説明図である。

【図２】実施例及び比較例で調製された不均質構造の CeO_2－ZrO_2 複合酸化物粒子の表面Ｃｅ量を示すグラフである。

【図３】実施例及び比較例の触媒の初期における飽和 NO_x 吸蔵量を示すグラフである。

【図４】実施例及び比較例の触媒の初期におけるＲＳ NO_x 吸蔵量を示すグラフである。

【図５】実施例及び比較例の触媒の耐久試験後における飽和 NO_x 吸蔵量を示すグラフである。

【図６】実施例及び比較例の触媒の耐久試験後におけるＲＳ NO_x 吸蔵量を示すグラフである。

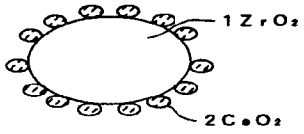
【図７】実施例及び比較例の触媒の耐久試験後における NO_x 浄化率を示すグラフである。

【図８】実施例及び比較例の触媒の耐久試験後におけるＨＣ排出量を示すグラフである。

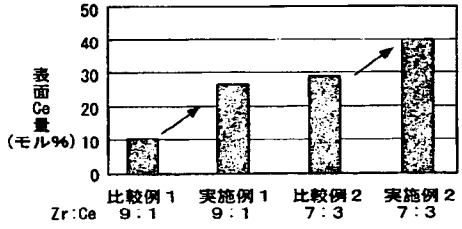
【符号の説明】

１：ZrO_2　　２：CeO_2

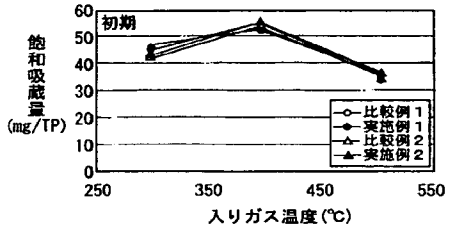
【図１】



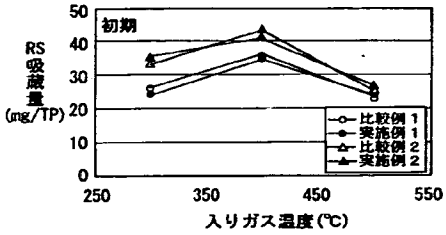
【図２】



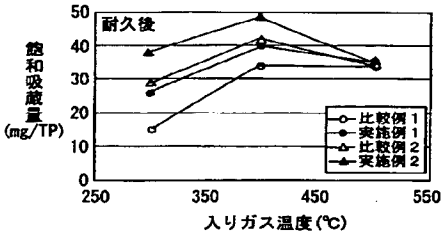
【図３】



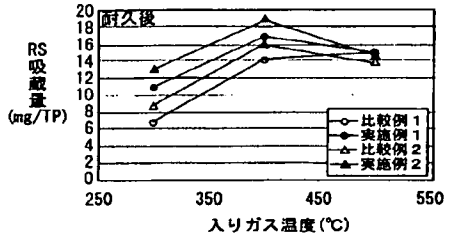
【図４】



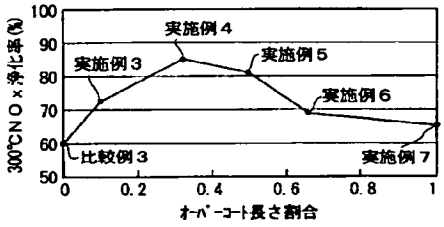
【図５】



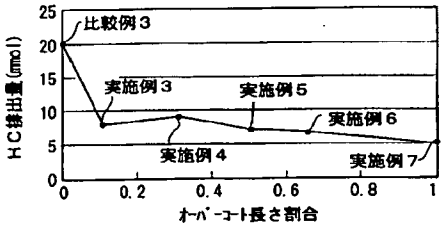
【図６】


耐久後
RS吸蔵量(mg/TP)
入りガス温度(℃)
比較例１
実施例１
比較例２
実施例２

【図７】


300℃NOx浄化率(%)
オーバーコート長さ割合
実施例４
実施例３
実施例５
実施例６
比較例３
実施例７

【図８】


HC排出量(mol)
オーバーコート長さ割合
比較例３
実施例３
実施例５
実施例６
実施例４
実施例７

フロントページの続き

(51)Int.Cl.[7]	F I	テーマコード（参考）
	B01D 53/36 102H	

Fターム(参考) 4D048 AA06 AA18 AB02 AB07 BA03X BA08X BA10X BA14X BA15X BA19X
BA30X BA31Y BA32Y BA33Y BA41X BA42X BB02 BB16 DA03 DA20
EA04
4G069 AA03 BA05A BA13B BB02A BB02B BB06A BB06B BC01A BC03B BC08A
BC13B BC38A BC43A BC51A BC51B BC69A BC75A BC75B CA03 CA09
EA19 EC29